Synthesis of Si-Y Coatings on Nb in Fluoride-Chloride Molten Salts

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A P Apisarov[1], A V Isakov[1], A A Chernyshev[1,2], A S Shmygalev[1,2], I A Vorotilov[3], V V Kashirtsev[3], O R Rahmanova[1,2] and Yu P Zaikov[1,2]

[1]Laboratory of Electrocrystallization and High Temperature Galvanotechnics, Institute of High Temperature Electrochemistry of UB RAS, 620990, Russian Federation
[2]Department of Electrochemical Production Technology, Ural Federal University, 620002, Russian Federation
[3]Department of Metals and Metallurgical Technologies, PJSC Kompozit, 141070, Russian Federation

E-mail: aac-vp@yandex.ru

Abstract. The preparation of multicomponent coatings based on silicon and yttrium on the niobium substrate was investigated. Y-Si/$NbSi_2$ coatings on the Nb substrate by currentless deposition in molten salts were produced. The preparation of $NbSi_2$ layers is carried out in NaF-NaCl-Na_2SiF_6 melts with the addition of Si powder. The preparation of Y-Si layers is carried out in NaCl-KCl-YF_3 melts containing Y powder. Coating samples are studied using SEM. It is established that sequentially synthesized coatings are characterized by a two-layer structure. Using the EDS method, the chemical composition of the obtained layers is established: Y – 26.68; Nb – 62.55; Si – 10.76 wt. %. The oxidation test of the obtained coatings Y-Si/$NbSi_2$ on Nb samples is performed. It is found that testing at 1200 ˚C for 2 hours leads to a mass loss of 62 mg/cm^2·h.

1. Introduction

High-temperature oxidation in gases and the study of protection methods against this phenomenon is a series scientific problem. A significant number of works is devoted to this item [1-3]. The driving forces are understood, the kinetic of the processes is found out, the basis of the gas corrosion theory is established. Sufficient materials are collected to predict the coatings formation mechanisms. The basis of the processes for the production of the highly-entropic alloys is created [3]. The formation of protective coatings is an important direction in the development of fundamental research. Protective coatings help to prevent or slow down the high-temperature oxidation [4-6]. Protection against the high-temperature oxidation is widely used in aerospace industry.

The electrochemical deposition of alloys without the use of electric current is a promising method for multicomponent coatings production. Methods for applying diffusion coatings in molten salts, as a rule, relate to simple equipment and do not require big expenses for the production of raw materials, even for the formation of coatings on the large products [7]. The processes of applying electrochemical diffusion coatings without the application of current depend on the ability of alloys formation and the difference in the electrochemical potentials of the elements.

The electrochemical method lacks several fundamental limitations. In contrast with the supersonic atmospheric plasma spray (SAPS), coatings can be applied to the inside of the product. Furthermore, in contrast with the halide activated pack cementation (HAPC), the hard-to-reach areas such as internal and external threads and capillary tubes can be machined. When using HAPC (the simultaneous saturation with at least two elements), several simultaneous processes are observed. The process of interaction of each element with a substrate (saturated metal) is accompanied by the processes of interaction of diffusion elements as with each other as with the activator [8].

It should be noted that the elemental composition is set by the method of coatings applying. A protective coating is formed only after several cycles of exposure to the high-temperature oxidation. The phase composition of the protective coatings differs from the initial ones. The layers having a complex oxide nature are formed. They prevent the oxidizing agent to the surface of the protective layer (e.g., intermetallic) and to the main metal to be protected.

Alloys based on Nb are wildly used in the space industry and aviation equipment. However, the protection against oxidation is required for the operation of niobium alloys at high temperatures in an oxidizing environment.

To date, the most effective coatings that protect against the oxidation are coatings which, when oxidized, form either a silicon oxide film or silicate phases on the surface [9]. Today, silicide coatings on niobium and its alloys are an independent protective coating. Silicide coatings can be the basis for the formation of complex protective structures (high-temperature structured materials) to prevent the oxidation. Niobium-silicide composites have a low density, high melting point, an excellent creep resistance (this is important for the flow operation) and stability at low temperatures [10-13].

Silicides form a SiO_2 protective film during oxidation. Many attempts have been made to synthesize alloys capable of forming a protective oxide film at high temperatures [14-17]. The main oxidation reaction is considered to be [18]:

$$4NbSi_2(s) + 13O_2(g) \rightarrow 8SiO_2(s) + 2Nb_2O_5(s) \quad (1)$$

The modified silica films in the form of silicates protect against the oxidation better. In contrast to the mixed complex oxides, the structure of silicates at higher temperatures is closer to the glass than to the crystal one. Accordingly, the doping of the protective coating will affect the glass transition temperature of the layer.

Yttrium silicates are the promising barrier layer. Yttrium silicate is characterized by the low vapor pressure at high temperatures [19], and the low oxygen permeability [20]. In [21], it was reported that the oxygen permeability of yttrium silicate is $1 \cdot 10^{-10}$ kg/m·s at 1700 °C. The phase formation in the yttrium oxide–silicon oxide system as applied to the protection of C/C and SiC/SiC composites was explained in detail in [22–24]. It was noted in reviews [23, 24] that yttrium silicates have a unique set of physicochemical properties (including high melting points). They are promising materials to be used as the high-temperature antioxidant coatings. This is based on a detailed study of the behavior of the Y_2O_3–SiO_2 system [25].

The presence of yttrium in the silicide alloy leads to the appearance of the film containing yttrium silicates. They can plasticize the film above a temperature of 1200 °C and, at the same time, reduce the vapor pressure above the film.

The present work aims to form the foundations of a sequential synthesis of coatings based on niobium silicides modified with yttrium by the electrochemical method without applying an electric current in molten salts. Coatings are created to protect against the oxidation at temperatures up to 1200 °C.

2. Experimental

2.1. Preparation of salts

The applying of protective coatings was carried out in molten salts. Compositions based on alkali metal fluorides containing silicon and yttrium compounds were selected to obtain coatings. The Nb cylinder with a diameter of 10 mm and a height of 20 mm was used as a substrate.

Obtaining of niobium silicide layers was carried out in the melt NaF-NaCl-Na_2SiF_6. Obtaining of Y-Si layers on the substrate from niobium silicides was carried out in the melt NaCl-KCl-YF_3. Mets were prepared from individual salts: the NaCl and NaF (99.9 wt. %), Na2SiF6 (99 wt. %) supplied by CJSC Vecton (St. Petersburg, Russia). The KCl (99.9 wt. %) supplied by PJSC Uralkali (Berezniki, Russia). YF_3 was synthesized from metallic yttrium. The sodium chloride, sodium fluoride, potassium chloride were dried in a glassy carbon crucible under vacuum at T = 923 K for 4 hours.

The sodium hexafluorosilicate was purified from the oxygen impurities by treating with the ammonium fluoride. The K_2SiF_6 was mixed with 2 wt. % NH_4F and sustained at 673 K for 6 hours in a glassy carbon crucible. The gaseous HF, released during the thermal decomposition of the ammonium fluoride, reacted with the oxide impurities contained in the Na_2SiF_6 with the formation of the gaseous compounds of silicon, ammonia, and water vapor.

YF_3 was synthesized in aqueous acid solutions. Metallic yttrium was immersed in a hydrochloric acid solution where YCl_3 was released according to the reaction:

$$2Y + 6HCl = 2YCl_3 + 3H_2\uparrow \quad (2)$$

Then, a concentrated hydrofluoric acid solution was added to an aqueous solution of YCl_3. After this, YF_3 deposit occurred according to the reaction:

$$YCl_3 + 3HF = YF_3\downarrow + 3HCl \quad (3)$$

Reaction (3) is carried out at a temperature of 80 °C. The resulting YF_3 deposit was washed with distilled water and dried. Drying was carried out at a temperature of 100 °C for 8 hours. Then the residual moisture was removed by evacuation at 200 °C for 16 hours. Next, YF_3 (99.9 wt.%) was used for the preparation of melts.

2.2. Electrochemical cell

The coatings were obtained in a water-cooled stainless-steel cell in an atmosphere of the high-purity argon (Figure 1). The retort was placed in a resistance furnace to provide temperature conditions. A container with a melt and coating samples was placed inside the retort. Y-Si/$NbSi_2$ coatings on a niobium substrate were obtained in two stages. The first stage is the siliconization of niobium. The second stage is a partial replacement of silicon in niobium silicide by yttrium. The compositions of the salt mixtures and temperature conditions are shown in Table 1.

Table 1. Conditions of coating production.

Stage	Melt composition, (wt. %)	Temperature, (°C)	Time, (h)	Coating thickness, (μm)
1	NaF(23.1)-NaCl(61.9)-Na_2SiF_6(10)-Si(5)	900	10	30
2	NaCl(50.4)-KCl(39.6)-YF_3(5)- Y(5)	875	5	30

Y and Si powders were used as the raw materials for maintaining the ion concentration. Powders were added to the melt in the form of fine powder.

Before starting the experiments, a mixture of salts was placed in a glassy carbon crucible to obtain niobium silicide. Next, the crucible was heated to the temperature of the experiment and the process was carried out. Addition of Y into the composition of $NbSi_2$ was carried out in a nickel container. Samples and NaCl-NaF melt with samples were placed in the container. Then the container was heated to process temperature. After that, a mixture of metallic yttrium and YF_3 was added in the required amount.

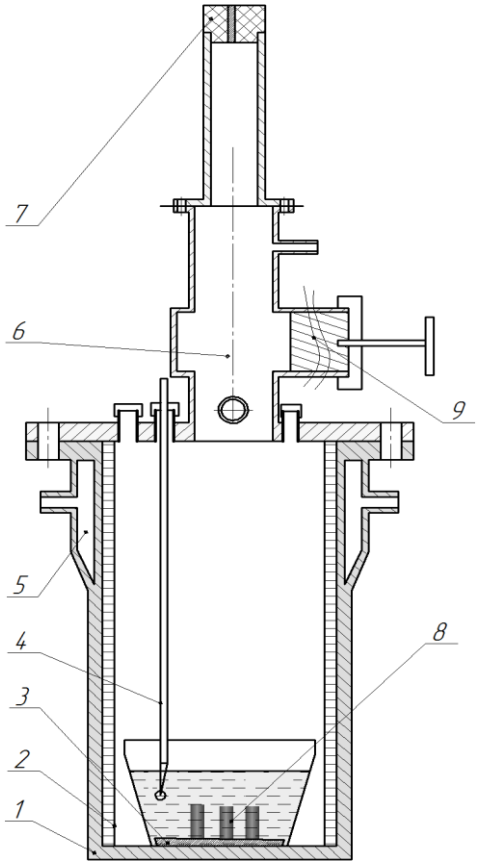

Figure 1. Scheme of cell for coating production: 1 – corrosion-resistance steel retort; 2 – nickel screen; 3 – yttrium or silicon powder (shavings); 4 – thermocouple; 5 – cooling jacket; 6 – cathode current supply; 7 – rubber seal; 8 – substrates; 9 – shutter.

Niobium cylinders with a diameter of 8 mm and a length of 15 mm were used as substrates. Semi-finished products $NbSi_2$/Nb (Table 1, stage 1) were used for modification by yttrium.

After the experiments, containers with frozen salts and samples were removed from the retort and the salts were separated using aqueous solutions of sulfosalicylic acid.

2.3. Oxidation test and Experimental techniques

During the production of the coating, the mass of samples was recorded before and after each stage. The obtained samples were tested for heat resistance at a temperature of 1200 °C for 2 hours. The studies were executed in a resistance furnace. Samples were placed in an Al_2O_3-based ceramic container.

The obtained coating samples were investigated. The metallography was carried out by scanning electron microscopy with the installation of micro-X-ray spectral analysis (EDS) on a JMS-5900LV instrument. Cross-sections observation was made using a Struers equipment complex.

The impurities determination in the deposits, electrolyte, and original salts was conducted by the atomic-emission method with inductively coupled plasma on the iCAP6300 Duo (Thermo Scientificinc, USA).

3. Results and discussion

3.1. Microstructure of As-Deposited coating

Sequential immersion of Nb samples in melts NaF-NaCl-Na_2SiF_6 and NaCl-KCl-YF_3 resulted in changing in appearance connected with the formation of a deposit. The results of the cross-sections observation study of the samples are presented in Figure 2a.

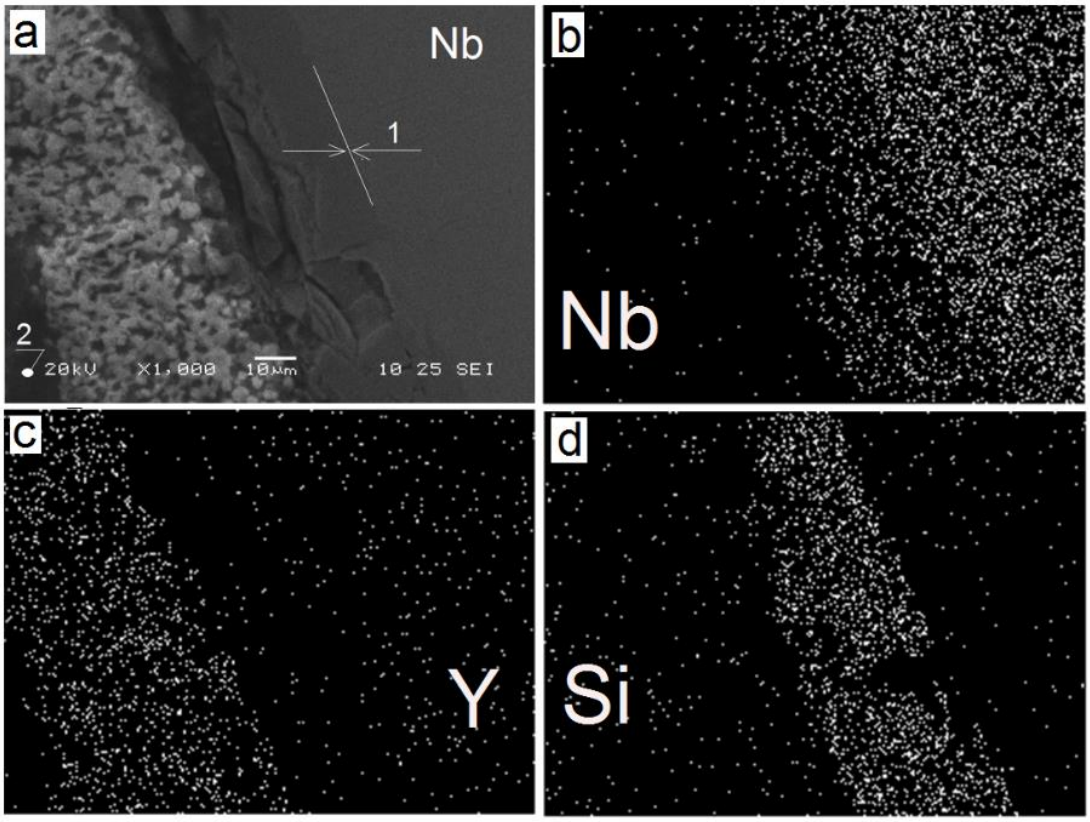

Figure 2. Data of scanning electron microscopy of the cross section obtained by silicone yttration: a - in direct electrons: 1 - interphase boundary; 2 - resin; b - Nb distribution; c - Y distribution; d-Si distribution.

According to the SEM data, two layers of the coating components can be distinguished. The layer adjacent to the niobium substrate is typical niobium silicide. That layer is more fragile than niobium. While polishing, it cracks. There is a clear boundary between the niobium silicide layer and the substrate. The second layer on the outside of the sample is also continuous. The second layer has a good adhesion to the first one. However, it is possible due to the difference in mechanical properties, the boundary between the first and the second layer crumbles during polishing.

Diffusion coatings are often characterized by an uneven distribution of elements. A map of the distribution of elements was created to determine the areas of concentration of the coating components. Data on the distribution of elements over the cross-section observation are presented in Figure 2 b, c, d.

The maps of the distribution of elements show that, as a result of the interaction, silicon penetrates the Nb substrate. Silicon atoms are distributed in the upper layer of the Nb substrate. Yttrium added by saturation in the NaCl-KCl-YF_3 melt is distributed at the external boundary of the coating.

The results show that in the first stage, the most probable process is the exchange one in the element:

$$Si|\ NaF\text{-}NaCl\text{-}Na_2SiF_6\ |\ NbSi\ |Nb \quad (4)$$

At the first stage, a coating is formed from niobium silicide. At the second stage, the process proceeds in the element:

$$Si|\ NaCl\text{-}KCl\text{-}YF_3|\ YSiNb\ |SiNb \quad (5)$$

Yttrium does not form alloys with niobium. That is why a sequential scheme of saturation with yttrium of the surface layer of a niobium substrate was chosen. At stage 2, the process proceeds in element (5). The driving force for the incorporation of yttrium into the coating of niobium silicide is the energy of the alloy formation of silicon and yttrium. When yttrium is introduced into a layer containing Si and Nb, an increase in the coating volume is likely to occur.

The chemical composition of these layers was determined using EDS. Data of EDS spectroscopy are presented in Figure 3.

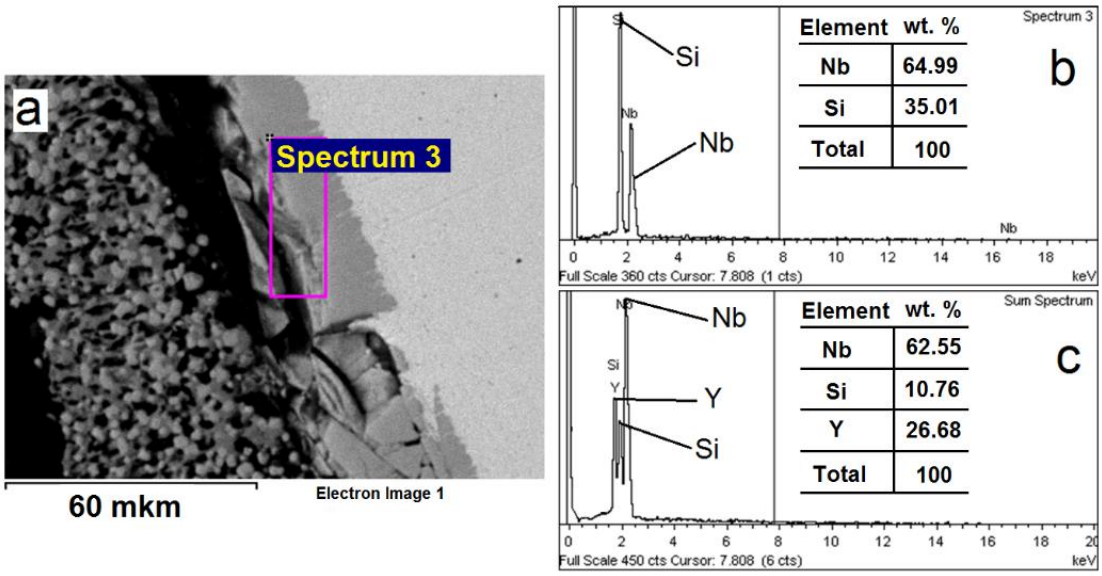

Figure 3. Typical EDS data of the sample cross section after coating production: a – investigation area; b – spectrum 3 from the area 3a; c – spectrum over the total area of Figure 3a.

According to the EDS results, it was found that the coating is a two-layer formation consisting of a $NbSi_2$ layer and a layer containing Y–Si alloy. Sequential deposition from molten salts makes it possible to obtain a coating with a chemical composition: Y – 26.68; Nb – 62.55; Si – 10.76 wt. %. This yttrium content should significantly affect the change in vapor pressure of silicon dioxide formed during the oxidation of the coating. Thus, during the successive immersion of Nb samples in NaF-NaCl-Na_2SiF_6 and NaCl-KCl-YF_3 melts, the chemical processes of the formation of niobium disilicide and Y-Si-Nb alloy depleted in niobium are sequential ones.

3.2. Oxidation test of coating

The obtained coating samples Y-Si/Nb_ySi_y/Nb are subjected to the high temperatures in an atmosphere of air in a bell-type resistance furnace with the disulfide-molybdenum heaters. Heating was carried out by the time dependence of the temperature shown in Figure 4a.

During the experiment, the sample was exposed to atmospheric oxygen. To minimize the possible effect of the difference in the coefficients of linear thermal expansion of the coating and the substrate, stepwise heating was performed. After exposure to temperature (Figure 4a), the overall view of the samples changed. A white-yellow film was formed on the surface. The typical SEM data for an oxidized sample is shown in Figure 4b.

The surface of the sample after oxidation had a layered structure and was formed by elongated crystals. It was established that the surface of the samples during oxidation was protected by a film, which included niobium silicate and silicon oxide containing yttrium. The overall view of the sample before and after the tests is shown in Figure 5.

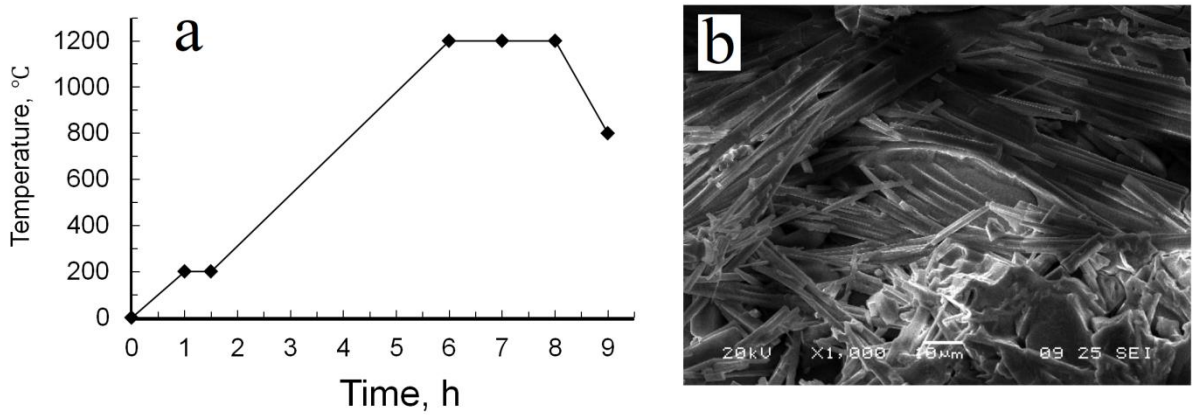

Figure 4. Oxidation test data of coating Y-Si/$NbSi_2$ on Nb substrate: a – temperature distribution during oxidation; b – SEM data of the sample surface after oxidation.

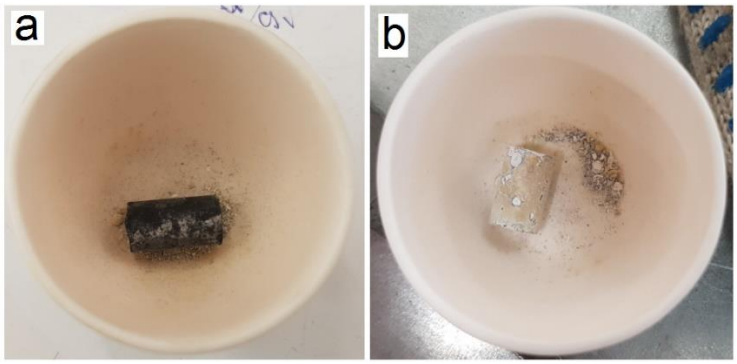

Figure 5. The overall view of the samples: a – before oxidation; b – after oxidation.

After oxidation (Figure 5b), a certain amount of crumbled coating was found in the container. The chipped pieces mainly contained silicon and oxygen. It was shown that during the test the sample lost 0.0059 gram of mass, which is 0.62 mg/cm^2·h.

4. Conclusion

The principal possibility of deposition of a two-layer protective coating based on silicon and yttrium by sequential currentless transfer in molten salts NaF-NaCl-Na_2SiF_6-Si and NaCl-KCl-YF_3-Y is shown. Coatings with a thickness of 30 μm are obtained. They consist of: Y – 26.68, Nb – 62.56, Si – 10.75 wt. %. The executed tests on heat resistance at 1200 °C for 2 hours showed a decrease in sample mass of 0.0059 g, which, in terms of specific characteristics, was 0.62 mg/cm^2·h. The obtained value of the mass loss per unit surface per hour can be considered to be satisfactory. It is possible to recommend silicon-yttrium coatings to protect niobium products in the oxidizing environment and temperatures up to 1200 °C.

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